Analysis of the Influence of Film-Forming Compounds on Droplet Growth: Implications for Cloud Microphysical Processes and Climate

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ABSTRACT

Decades of cloud microphysical research have not provided conclusive understanding of the physical processes responsible for droplet spectral broadening. Numerous mechanisms have been proposed—for example, entrainment mixing, vortex shedding, giant cloud condensation nuclei (CCN), chemical processing of CCN, and radiative cooling—all of which are likely candidates under select conditions. In this paper it is suggested that variability in the composition of CCN, and in particular, the existence of condensation inhibiting compounds, is another possible candidate. The inferred potential abundance of these amphiphilic film-forming compounds (FFCs) suggests that their effect may be important. Using a cloud parcel model with a simplified treatment of the effect of FFCs, it is shown that modest concentrations of FFCs (on the order of 5% of the total aerosol mass) can have a marked effect on drop growth and can cause significant increases in spectral dispersions. Moreover, it is shown that FFCs may, in some cases, reduce the number concentration of cloud droplets, with implications for cloud-climate feedbacks. This trend is at least in qualitative agreement with results from a recent field campaign.

1. Introduction

For more than 50 years a common theme in many warm rain cloud microphysical studies has been the inability of cloud models to explain the breadth of droplet spectra that are observed in natural clouds. The comparison between observations and model simulations is difficult because droplet spectrometers are not free of error (e.g., Baumgardner et al. 1985) and also because of artifacts that are often an integral part of numerical models. The forward-scattering spectrometer probe (FSSP) is one of the primary instruments used to measure cloud droplet size spectra and it suffers from numerous problems, including inhomogeneity of the laser beam, which causes sizing errors when droplets pass through different regions of the beam; coincidence errors; nonmonotonic responses of Mie scattering to droplet size; and others. Nevertheless, the plethora of studies on the subject tends to point to the fact that the disparity in spectral breadths is likely a real one (Hudson and Yum 1997).

A large body of literature exists regarding the variety of mechanisms that might account for this disparity. These are mentioned only briefly without comment on their relative importance.

It has been suggested that entrainment mixing, either homogeneous (e.g., Warner 1969), or inhomogeneous (Baker et al. 1980) can broaden spectra through small-scale turbulence and associated fluctuations in supersaturation. In the homogeneous mixing scenario, dry air mixes with cloudy air and the affected volume experiences evaporation of all droplets (the timescale for mixing is shorter than that for evaporation). This produces only slight broadening. The inhomogeneous mixing hypothesis suggests a multistage mixing process, the result of which is a bimodal droplet spectrum similar to that found in some observations, with dispersion increasing with height above cloud base.

Recently, Shaw et al. (1998) proposed that vortex structures in the turbulent cloud can fling droplets out of regions of high vorticity into regions of high strain. These local variations in drop concentration (at the centimeter scale) create a supersaturation field that varies with droplet density, allowing droplets in low concentration zones to grow more rapidly. Calculations indicate significant broadening.

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Longwave cooling of water droplets at the tops of stratiform clouds and fog layers has been suggested as a mechanism for the production of large droplets (e.g., Roach 1976). Net radiative cooling of the droplets allows the latent heat of condensation to be dissipated more rapidly than when cooling is absent. The effective saturation felt by a drop is larger than that calculated without this effect; the enhancement in saturation increases with increasing drop size. Not only is the growth of larger drops enhanced, but for a weakly convective cloud, large drops that experience supersaturated conditions may grow at the expense of smaller ones that experience subsaturated conditions (Harrington et al. 2000). Broadening may therefore occur toward both the large- and small-drop ends of the spectrum.

Zhang et al. (1999) showed that the addition of sulfate mass to droplets as a result of heterogeneous chemical processing may enhance the ability of large drops to grow, and in some processing scenarios broaden the drop spectrum. There, too, it was found that under weak convective conditions, the enhanced solute effect resulting from processing may allow large drops to grow at the expense of small ones.

Finally, the existence of even small concentrations (order of 1^{-1}) of giant or ultragiant cloud condensation nuclei (CCN; radii $> \approx 1$ μm) that quickly achieve radii of 20 μm in humid conditions can initiate spectral broadening through collision coalescence (e.g., Johnson 1982; Feingold et al. 1999). This mechanism differs from the others in that it invokes droplet collision coalescence, rather than condensation growth, to explain broadening.

This paper does not dispute these works, nor does it attempt to ascertain their relative importance. Instead it focuses on an alternative mechanism which has not been widely considered. The main idea is that some amphiphilic organic compounds [that we will term film-forming compounds (FFCs)][1] can form compressed films on the surface of droplets, and that this coating may inhibit droplet growth for long enough that some fraction of droplets grow in conditions of relatively high supersaturation and they achieve larger sizes than they would have, had the entire population of drops been growing simultaneously. By the time the film on the haze droplets is reduced to less than a complete monolayer, and these drops can thereafter grow freely, the size spectrum is significantly broader than that achieved in FFC-free conditions.

We stress that this study is exploratory in nature and somewhat speculative in that little is known about the abundance, nature, and distribution of FFCs in atmospheric aerosol. Nevertheless, we feel it is important to explore the possible effects of these FFCs using some reasonable assumptions.

In section 2 we consider the evidence for organic FFCs and review the literature on the subject. Section 3 describes the numerical model used in this study and the assumptions made to represent FFCs. We then explore conditions under which FFCs either produce significant broadening, or have no effect at all (section 4). Finally we consider some implications for this broadening, and an often concomitant suppression in drop number concentration.

2. Evidence for film-forming compounds

It has been argued that ''organic films are probably common on atmospheric aerosol particles'' (Gill et al. 1983). The existence of compressed films on sea salt droplets was deduced by Blanchard (1964). Husar and Shu (1975) presented electron micrographs of Los Angeles haze particles, which suggest that the particles were coated with a nonvolatile film.

Laboratory experiments have shown that compressed surface films of certain organic compounds can retard evaporation and/or condensation of water from flat surfaces (e.g., Barnes 1986; McNamee et al. 1998) and droplets (Snead and Zung 1968; Garrett 1971; Rubel and Gentry 1984; Otani and Wang 1984; Seaver et al. 1992; Xiong et al. 1998), although the mechanism for such retardation remains unconfirmed. The magnitude of the effect also varies depending on the technique and compounds used. One interesting finding regarding surface films is that they alter the kinetics of mass transfer, but not the equilibrium; that is the equilibrium vapor pressure of a liquid water surface is unchanged by the presence of a surface film (Barnes 1986).

A substantial fraction of the studies used cetyl alcohol (hexadecanol), with some of the investigators deducing condensation coefficients for such droplets to be on the order of 1×10^{-5}. Although cetyl alcohol may not be present in large quantities in the atmosphere, it is used here as a proxy for other possible film compounds. In nature, multiple-compound films are likely, but these have barely been studied in any setting. Presumably, some compounds will form films that are more permeable than cetyl alcohol, and some less. The abundance of these compounds is not known so it is hard to predict what will occur in nature. We therefore selected the best-studied compound. Studies of a man-made fog (Kocmond et al. 1972) with and without cetyl alcohol show reduced formation and dissipation rates when the alcohol is added. Bigg et al. (1969) conducted field experiments that yielded results that are consistent with reductions in fog formation by using a mixture of cetyl alcohol and octadecanol. Bigg (1986) reported that the formation of droplets in a cloud condensation nucleus counter-exhibited a time dependence; sometimes a cloud of droplets was formed quite quickly ($\approx$1 to 2 s), while on other occasions up to 30 s was required. This suggests

[1] Many authors use the term ''surfactant'' to describe these condensation-inhibiting surface films. We note that this is not strictly correct since the common definition of a surfactant is an agent that reduces surface tension, a phenomenon not necessarily associated with the compounds described here. For this reason we prefer to use the term FFC.

that the rate of condensational growth of some particles is substantially reduced, possibly due to the presence of surface films.

A few, limited studies have examined the potential effects of surface films on cloud formation. Podzimek and Saad (1975) presented one example of the growth of cetyl alcohol–contaminated particles and showed that cloud supersaturation can be significantly larger than that in an FFC-free case. In their simulation, the distribution of FFC was such that the smallest class of CCN grew faster than larger CCN because its film was broken before those of the larger particles. They concluded that the effect of FFC was strongly dependent on the amount of FFC, its distribution among particles, the extent to which the condensation coefficient was modified, the size distribution of CCN, and the updraft velocity. Derjaguin et al. (1985) performed a single simulation that showed that cetyl alcohol can retard the growth of a significant fraction of CCN, drive up supersaturation, and separate the spectrum into a mode of actively growing droplets and a mode of small droplets exhibiting retarded growth. They suggested that this mechanism could enhance rainfall production.

The aforementioned studies suggest that a more rigorous exploration of the conditions under which FFCs might have an effect on drop spectral evolution is in order. The current study can therefore be viewed as an extension of these works to a much broader phase-space, with the addition of a detailed analysis to better understand the model results, and an attempt to understand the implications for drop spectral broadening and climate.

3. The numerical model

A parcel model adapted from Feingold and Heymsfield (1992) is used. For a prescribed rate of adiabatic ascent, the model calculates the uptake of water vapor by a size distribution of aerosol particles, their subsequent activation, and growth by condensation using the variable coefficient ordinary differential equation solver (VODE; Brown et al. 1989). Although the model has been adapted to represent entrainment by diluting the total cloud water, the rather ad hoc way this is done is not deemed sufficiently realistic to warrant including entrainment effects. Moreover, because there is some evidence that spectral broadening may exist within adiabatic cores of cumulus clouds (Lasher-Trapp and Cooper 2000) the adiabatic framework would seem to be a reasonable starting point. In the current work the vertical velocity w is assumed to vary over the range $20 \leq w \leq 300$ cm s^{-1}. Droplet growth is solved following Pruppacher and Klett (1997, p. 509), assuming a thermal accommodation coefficient of unity. The particles are assumed to be partially soluble and composed of 50% ammonium sulfate (by mass) and 50% of an unspecified nonhygroscopic material, some fraction of which is FFC (see below). Aerosol size distributions are parameterized by a lognormal function (e.g., Jaenicke 1993) with respect to aerosol particle radius and defined by three parameters: r_g, the median dry radius; σ, the geometric standard deviation; and N_a, the total particle concentration. These parameters have been varied over a broad range of parameter space to represent a variety of scenarios (Table 1):

TABLE 1. Lognormal input parameters and updraft velocities for the model.

N_a (cm^{-3})	r_g (μm)	σ	w (cm s^{-1})
50	0.03	1.3	20
100	0.04	1.4	50
250	0.05	1.5	75
500	0.06	1.6	100
1000	0.07	1.7	150
	0.08	1.8	200
	0.09	2.0	300
	0.10	2.2	

$$0.03\ \mu\text{m} \leq r_g \leq 0.10\ \mu\text{m};$$

$$50\ \text{cm}^{-3} \leq N_a \leq 1000\ \text{cm}^{-3};$$

$$1.3 \leq \sigma \leq 2.2. \quad (1)$$

It is not suggested that the size spectra defined by (1) are true to natural size spectra but they do represent some basic important parameters, namely, size of particles, spectral breadth, and concentration. The spectra are represented by 100 discrete sizes and the growth of these particles due to uptake of water vapor is calculated on a moving grid to eliminate numerical diffusion. The spectra are truncated at lower and upper radii of 0.01 μm and 1 μm and thus do not represent giant CCN.

a. Modeling the effect of film-forming compounds on α

The condensation coefficient α is assumed to be 0.042 (e.g., Chodes et al. 1974; Shaw and Lamb 1999) for all simulations for which particles are assumed to be free of FFCs. Based on the studies surveyed in section 2, we simulate the effect of FFCs as a step increase in α from a small number ($\alpha = 10^{-5}$) when the haze particle is covered by enough molecules of FFC to constitute a monolayer, to $\alpha = 0.042$ when the number of molecules of FFC is insufficient to comprise a complete monolayer. For the assumed FFC, cetyl alcohol (1-hexadecanol, molecular weight 242), this step occurs when the surface area occupied per cetyl alcohol molecule is greater than 22 Å^2.

b. Distribution of the FFC mass among particles

The total mass of FFC is prescribed as a percentage of the total aerosol mass; values used here range from 2% to 10%. This range was chosen somewhat arbitrarily. Below 2% there is not much effect on drop growth so this is a useful lower bound. For an upper bound, we considered the fact that in analyses of aerosol samples,

a large fraction of aerosol remains unaccounted for. This fraction is much more than 10% but 10% seems to be a reasonable upper limit. The FFC is assumed to have entered the particles via a surface process, and therefore the mass of FFC is weighted by the original surface area of the aerosol population. This method is appropriate if the FFC comes from the gas phase and is deposited on the surface as secondary aerosol mass. An alternative would be to assume that the FFC comprises a constant percentage of the particle mass, regardless of size. This would be appropriate when particles are the product of a source that emits particles of constant composition. Although we have explored this avenue, in the interests of brevity, these results will not be shown here. Section 4c will briefly discuss similarities and differences from the main results. Other means of distributing FFC among particles are possible, but the exploratory nature of this study suggests that we await proper characterization of these compounds before pursuing more complicated scenarios.

4. Results

Results are presented by comparing the simulation output for two cases that are identical except that one assumes no FFC present, and the other adds some FFC. Unless otherwise stated, the total mass of FFC is 5% of the total aerosol mass. A given set of simulations comprises 2240 individual simulations for the range of aerosol size parameters and vertical velocities defined in Table 1. Additional sets of simulations are derived by varying the amount, or distribution of FFC among particles. Each parcel model simulation proceeds until the cloud water content LWC = 0.5 g m^{-3}, and comparisons between sets of simulations are performed at this point. A number of measures of drop spectral characteristics are used to compare base-case simulations with those affected by FFCs:

1) N_d is the number concentration of droplets having radii ≥ 1 μm;
2) $r_{\min}$ is the minimum radius of droplets with radius ≥ 1 μm;
3) $r_{\max}$ is the maximum radius of droplets having a concentration greater than 1×10^{-3} cm^{-3} [this condition is applied to avoid misleadingly high values of $r_{\max}$ for negligibly small concentrations of drops; a concentration of 1×10^{-3} cm^{-3} is also the approximate concentration of drops of radius 20 μm required to initiate significant collision coalescence (e.g., Feingold et al. 1999)];
4) $n(r)$ is the size distribution of drops in the range $r_{\min} \leq r \leq r_{\max}$;
5) D is relative dispersion defined as the ratio of the standard deviation of $n(r)$ to the mean droplet radius (unitless); and
6) r_e is the effective radius (ratio of third to second spectral moments).

Similar definitions are used for simulations that include FFCs with the addition of a subscript ''(s)'', for example, $r_{\min(s)}$, $r_{\max(s)}$, $D_{(s)}$, $N_{d(s)}$, and $r_{e(s)}$.

a. General trends

Figure 1 shows scatterplots of various parameters relative to their base case (no FFC) counterparts. It can be seen that the existence of FFC generally results in smaller $r_{\min}$ and in larger $r_{\max}$, indicating that spectral broadening occurs toward both the smaller- and larger-drop ends of the spectrum. The result is that the relative dispersion D is almost always greater when FFCs are present, sometimes by more than an order of magnitude. The FFC tends to suppress drop number concentration $N_{d(s)}$, and maximum supersaturation S_s tends to be higher than S because growth is retarded and $N_{d(s)}$ is reduced. Note too the consistency between the suppression of $N_{d(s)}$ and the increase in $r_{e(s)}$. There are also many instances when the FFC does not modify these parameters, as indicated by the proliferation of points along the 1:1 line. There also exist a few points for which dispersion is reduced by FFCs, but since these occurrences lie below the 10th percentile (Fig. 2), we do not focus on them. Figure 2 shows that in the mean, the enhancement in dispersion decreases with increasing N_a, and increases with increasing r_g, σ, and w. Horizontal bars indicate the 10th and 90th percentiles; thus the points located between these horizontal bars represent 80% of the model output. Figure 3 indicates that in the mean, FFCs result in a suppression of drop concentration, particularly at higher σ and r_g, and to a lesser extent at higher N_a and w. The fact that the enhancement in dispersion decreases with increasing N_a, and that drop number suppression increases slightly with increasing N_a suggests that the two effects are not necessarily correlated.

Measurements of N_d are often compared with those of aerosol concentration N_a (or some subset thereof). Figures 4a and 4b show model output of N_d versus N_a for cases both with and without FFC. The presence of FFC results in a reduction in the mean power of an assumed power-law dependence of N_d on N_a (0.87 versus 0.93). Also notable is an increased variability in the simulations with FFC (compare Figs. 4a and 4b), particularly in the regime of decreased N_d. This result is in contrast to a system where CCN exhibit diminished surface tension (Facchini et al. 1999), which would result in increased N_d. Figure 4c is a compilation of observations of N_d (measured by an FSSP) and N_a (measured by optical probes) derived from a variety of experiments and locations (Chuang et al. 2000; Martin et al. 1994; Leaitch et al. 1996; Raga and Jonas 1993). Note that in Figs. 4a and 4b, N_a is defined as all aerosol particles above 0.01-μm dry diameter; whereas, in Fig. 4c, N_a is defined as those particles measured by a passive cavity aerosol spectrometer probe (PCASP) with an approximate lower limit of 0.1 μm at ambient (below

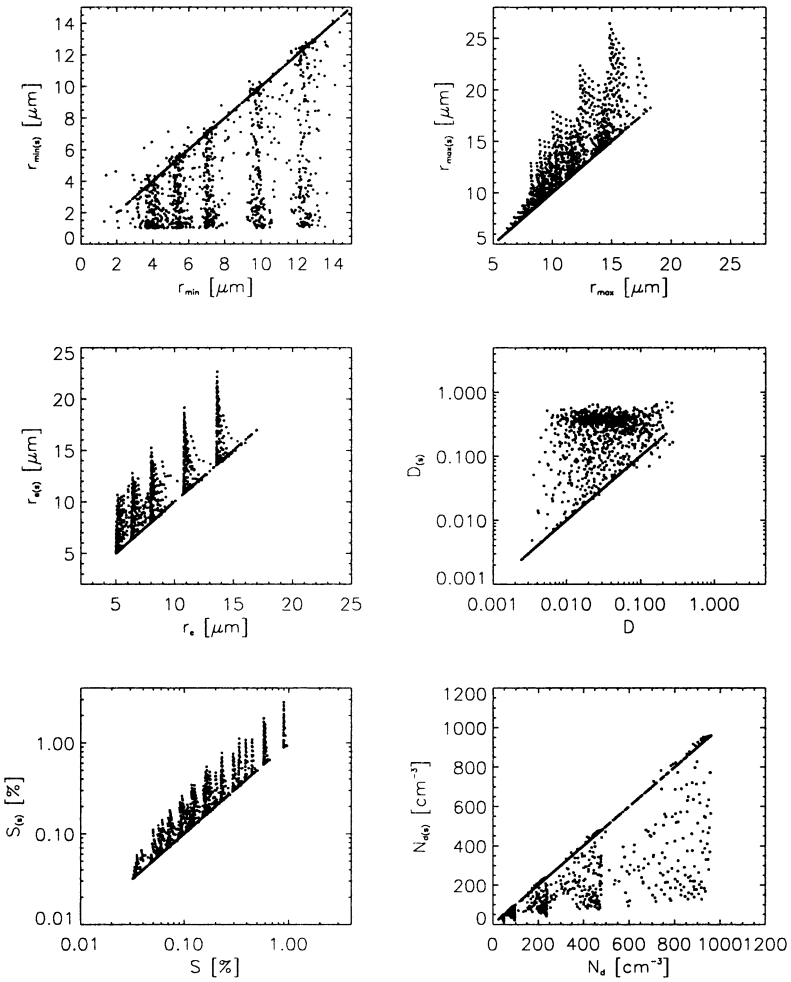

FIG. 1. Comparisons between FFC modified simulations [subscript (s)], and standard parcel model simulations at the end of the simulation (LWC = 0.5 g m^{-3}). Parameters are defined as follows: r_{min} is the minimum droplet radius >1 μm, r_{max} is the maximum droplet radius for which drop number concentration is $>1 \times 10^{-3}$ cm^{-3}, r_e is the effective radius, D is the relative dispersion of the drop spectrum, S is peak supersaturation, and N_d is total droplet concentration for $r_{min} \leq r \leq r_{max}$. The subscript (s) refers to FFC simulations. FFC contributes 5% to the total aerosol mass and is weighted by surface area. The accommodation coefficient α experiences a jump from $\alpha = 1 \times 10^{-5}$ to 0.042 when the monolayer ceases to exist.

cloud) RH. The comparison is made to show that the slope of the curve with FFC more closely matches the observations than the curve without FFC. This comparison is complicated by entrainment and other processes that make real clouds deviate from ideal adiabatic parcels, although the net effect this would have on the slope of the N_d versus N_a relationship is unclear. The variability in the FFC simulation cases is also more in line with observations. Note that the comparison of the absolute values of N_d versus N_a is not valid because of the different definitions of N_a, but this does not affect our primary argument as we only seek to show that the model simulations with FFC are not unrealistic given the set of available observations, and appear to be more reasonable than the cases without FFC.

b. Details for individual cases

Droplet spectra for individual simulations for which $N_a = 250$ cm^{-3}, $r_g = 0.08$ μm, $\sigma = 1.7$, and $w = 200$ cm s^{-1} are shown in Fig. 5a at the end of the simulation (112 s). These are conditions under which enhancement in D has been calculated. Spectra have been created from the discrete point model output by sampling to the size grid of an FSSP. The grid is defined by 1 μm $< r <$ 25 μm with a bin width of 1 μm. The surface area–weighted FFC mass distribution exhibits a relatively flat section below the modal radius that is qualitatively similar to some observations (e.g., Noonkester 1984, Figs. 4 and 6; Nicholls 1984; Curry 1986; Gerber 1996, Fig. 7). It is significantly broader than the case in which

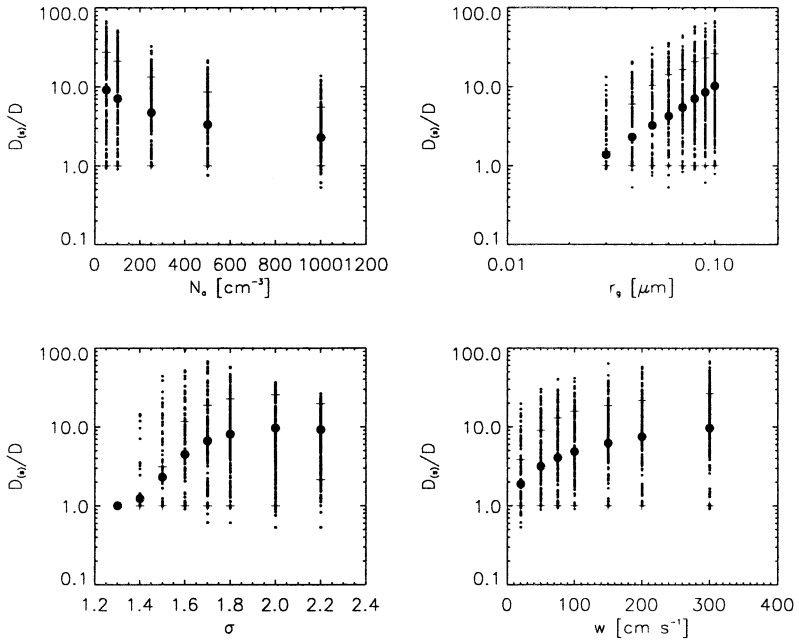

FIG. 2. Modification in dispersion related to FFC as a function of dry aerosol lognormal size parameters N_a, r_g, and σ, and vertical velocity w. Conditions are the same as in Fig. 1. The large filled circles represent the mean value, and horizontal bars, the 10th and 90th percentiles.

particles are unaffected by FFCs. Figures 5b and 5c reproduce some measured spectra from Noonkester (1984) and Gerber (1996) and indicate qualitative similarity with the FFC-affected spectrum in Fig. 5a. Note that the observed spectra derive from a variety of locations, and are characterized by different LWC so that comparison is only qualitative. Gerber refers to the flat part of the spectrum as ''nongrowing'' droplets (or haze particles), which is consistent with our conceptual view and calculations of how FFCs might affect droplets.

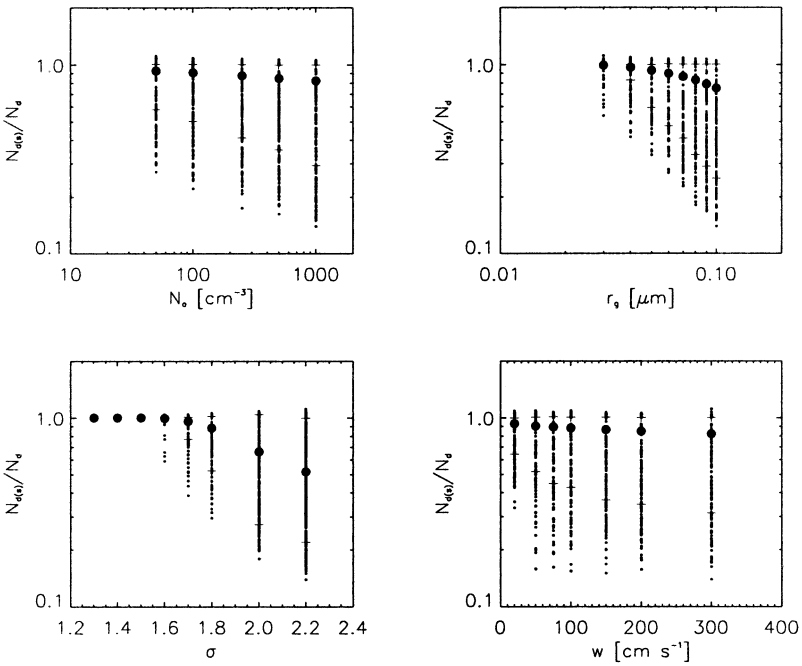

FIG. 3. As in Fig. 2, but for modification in drop number concentration.

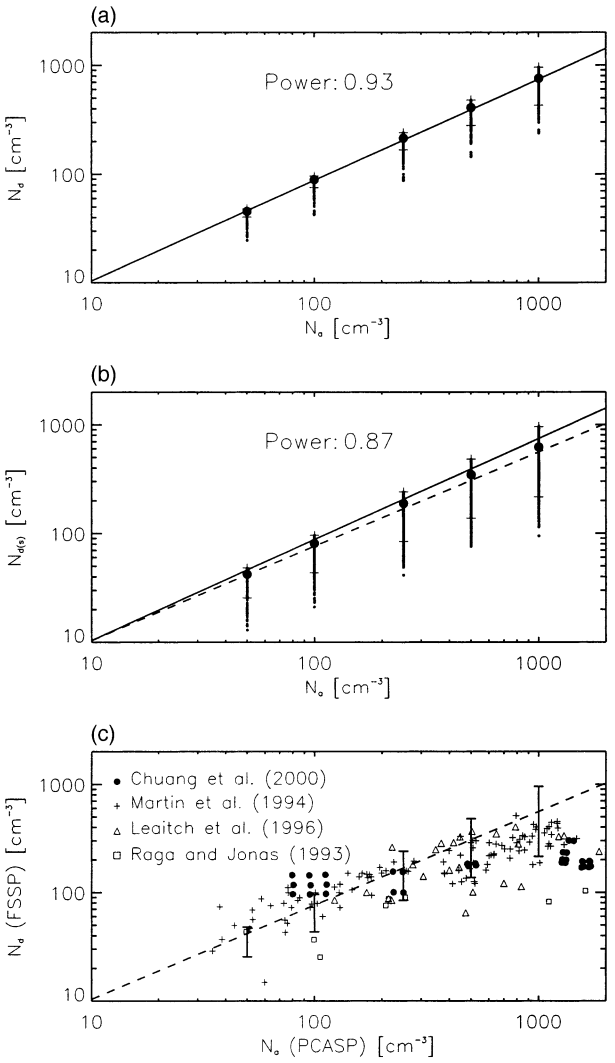

FIG. 4. Drop concentration N_d as a function of aerosol concentration N_a (a) for the case free of FFC, and (b) for the case with FFC as described in Fig. 1. The best-fit lines indicate that in the mean, FFC tends to suppress drop concentration. The solid lines pertain to the case without FFC and the dashed line to the case with FFC. Horizontal lines are drawn at the 10th and 90th percentile values. (c) Observations of N_d vs N_a after Chuang et al. (2000), Martin et al. (1994), Leaitch et al. (1996), and Raga and Jonas (1993). The dashed line is the same as in (b); vertical lines indicate the extent of the 10th and 90th percentiles in (b). Note the tendency for saturation in N_d at large N_a.

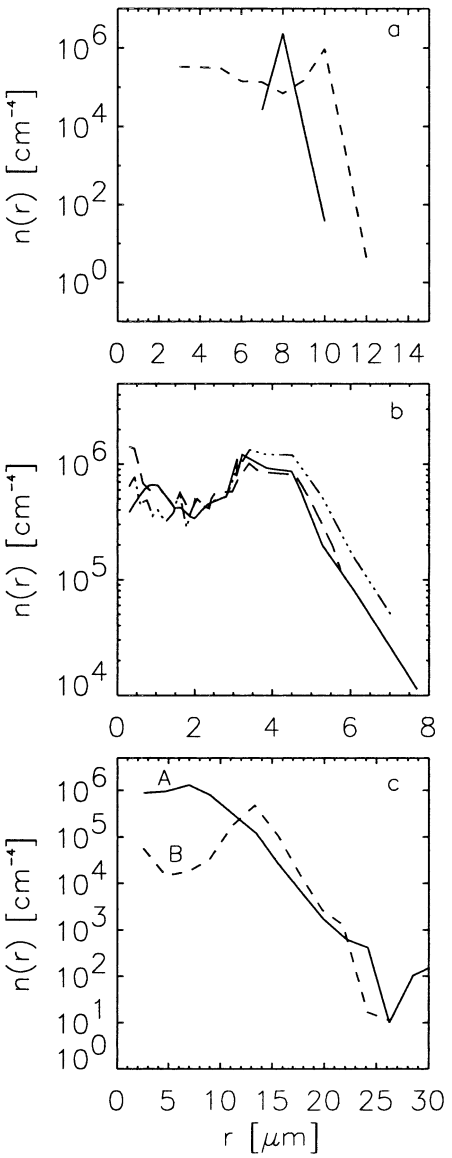

FIG. 5. (a) Comparison between simulated drop spectra as sampled on an FSSP size grid for individual simulations for which $N_a = 250$ cm^{-3}, $r_g = 0.08$ μm, $\sigma = 1.7$, and $w = 200$ cm s^{-1}. The solid line is for the FFC-free simulation and the dashed line for the simulation with FFC. Both spectra have an LWC $= 0.5$ g m^{-3}. (b) Cloud droplet spectra after Noonkester (1984) measured with a Particle Measuring System Inc. ASSP-100 (size range 0.23 μm $\leq r \leq$ 14.7 μm) about 35 m above the base of marine stratus clouds. (c) Cloud drop spectra after Gerber (1996) measured with an FSSP during the Atlantic Stratocumulus Transition Experiment (ASTEX) in 1992. The spectrum marked A is from a polluted air mass, and the one marked B is from a relatively clean marine air mass.

Note that Gerber's polluted spectrum is broader than the cleaner spectrum (see also, Hudson and Yum 1997). This may result from the fact that the growth per individual drop is less when the drop concentration is higher so that condensation produces less spectral narrowing.[2] Alternatively it may be due to the presence of larger, faster growing particles in the polluted spectra. More rigorous comparison with observations seems inappropriate without measurements of particle composition, and identification of the presence (or absence) of FFCs.

Figure 6 examines more closely the evolution of the drop spectra to their final forms as depicted in Fig. 5a.

[2] In this work we have used the dispersion D of the number distribution as a measure of the spectral breadth and therefore condensation results in a narrowing of the distribution. Note however that if breadth is considered with respect to surface area, condensation does not cause narrowing. All references to narrowing herein pertain to decreases in D.

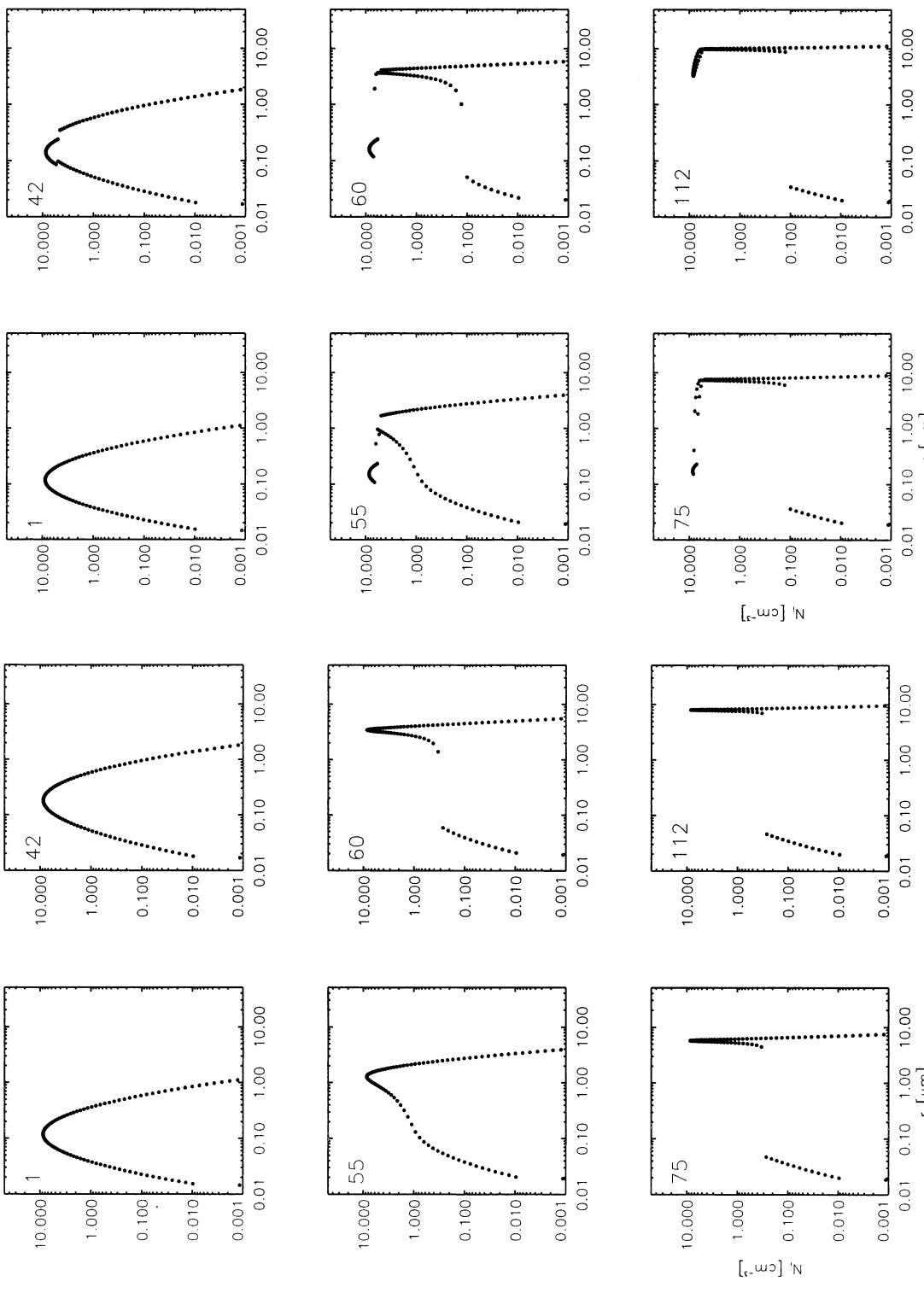

FIG. 6. Droplet growth as a function of time (in seconds, indicated at upper left) for (a) the FFC-free case, and (b) the case with FFC distributed as described in Fig. 1. Points pertain to the raw model output of drop concentration in size category i (denoted N_i). Note the rapidly narrowing drop spectrum after 60 s in (a). FFC retards growth of a large number of drops and enables the smaller and larger drops to grow and create the initial drop spectrum (at about 60 s). Later, FFC-laden drops near the aerosol mode break their monolayers and grow to join the initial drop spectrum (75–112 s).

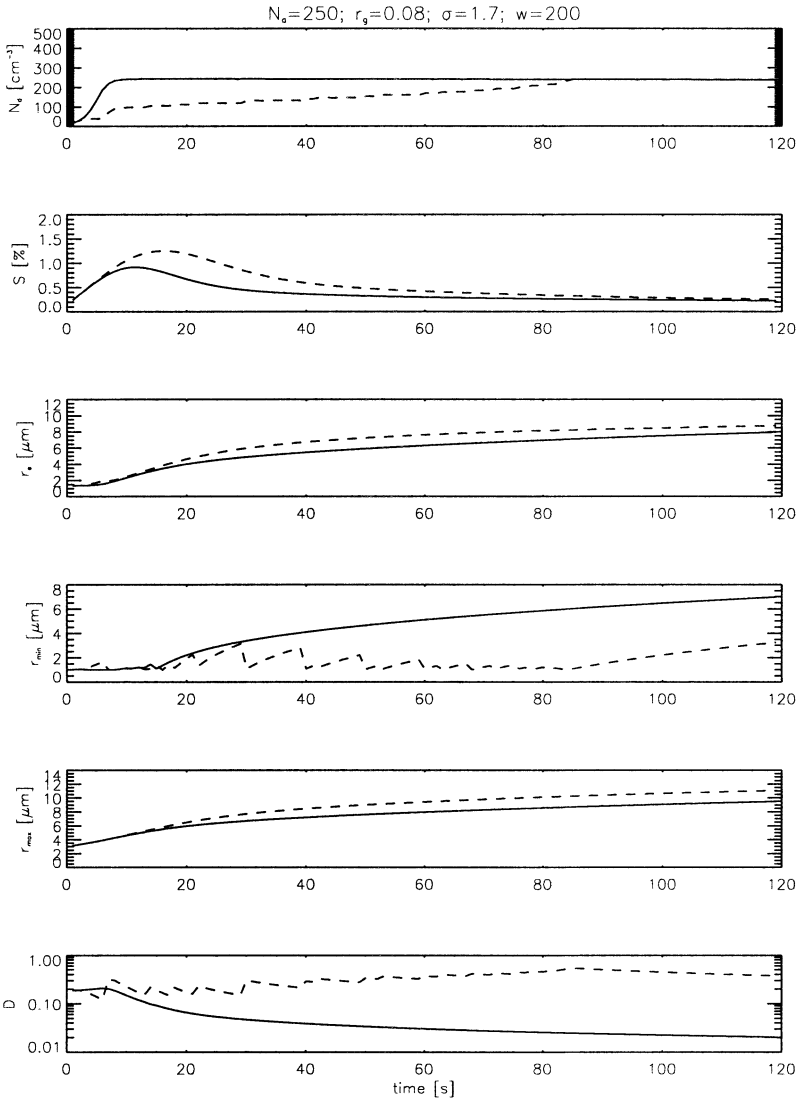

FIG. 7. Temporal evolution of various parameters for the simulations described in Figs. 6a and 6b. Solid lines are for the FFC-free simulation; dashed lines are for the simulation with FFC and the conditions described in Fig. 1.

Without FFCs (Fig. 6a), whether particles are to become drops is determined during some small window of time, and thereafter drops grow in unison with concomitant narrowing of the spectrum. However, with FFCs, Fig. 6b indicates that in the early stages of cloud formation, a significant subpopulation of particles (i.e., those near the surface area modal radius) are unable to grow because of their film coatings. This allows both smaller and larger particles to grow much more rapidly than they would if these particles had been competing for vapor. Smaller particles *overtake* those whose growth is hindered and join larger particles to form the initial drop spectrum. As time progresses, FFC-laden particles are able to take up some water until their monolayers break; at this point they grow rapidly toward the existing droplet spectrum. Together they form the drop spectrum (Fig. 5a) that exhibits a characteristic flat tail comprising particles that are relative newcomers to the droplet population and the modal radius that comprises drops that grew earlier in the process.

A sampling of numerous other individual spectra shows that this is the primary reason for spectral broadening for the conditions studied here. It raises the intriguing possibility that if FFCs do indeed act in this manner, there is not necessarily a 1:1 correspondence between aerosol size and drop size (see also Podzimek and Saad 1975).

Figure 7 shows time series of various parameters for the base case and FFC simulations corresponding to Fig. 6. From early on in the simulation, D_s maintains a large value, but exhibits periodic oscillations. This is due to the discrete nature of the model representation of the

aerosol spectrum. It reflects the fact that as individual size categories are freed of their monolayers and grow toward the drop spectrum, they enhance D_s. Until the next size category of particles experiences a break in its monolayer, the spectrum tends to narrow. These oscillations are therefore well correlated with oscillations in $r_{\min(s)}$. In addition to significant enhancement in D_s, this case also exhibits a strong suppression in $N_{d(s)}$ during the early stages of spectral evolution. However, $N_{d(s)}$ increases steadily and equals that of N_d at the end of the simulation. The lower $N_{d(s)}$ initially allows $S_{(s)}$ to build up, but as with N_d, the differences between S and $S_{(s)}$ are negligible by the end of the simulation. The enhanced $r_{\max}$ and r_e, and suppressed $r_{\min}$, that were evident in Figs. 1 and 5 are shown to be a consistent feature for the duration of the simulation.

Under some conditions, a strong suppression in $N_{d(s)}$ accompanies the enhancement in D_s for the duration of the simulation. For example, when $N_a = 250$ cm^{-3}, $r_g = 0.08$ μm, $\sigma = 2.0$, and $w = 200$ cm s^{-1}, drop number concentration is reduced to less than half, and $r_e = 15$ μm at the end of the simulation (figure not shown). This value is close to that often assumed to be the point at which drizzle ensues (e.g., Gerber 1996).

c. FFC weighted by particle mass

Similar simulations to those in sections 4a and 4b, but with the FFC weighted by particle mass, have been performed, but only key results and differences are mentioned. The mass weighting of FFC primarily inhibits the larger aerosol sizes from growing, and smaller particles, which break their monolayers sooner, quickly overtake the large particles. As time proceeds, larger particles do begin to grow but they cannot catch up to the sizes they would have achieved in the absence of FFC. Maximum drop size is therefore reduced rather than enhanced as was the case in Fig. 5a. The growth of these larger particles at a later stage tends to create a tail of smaller droplets similar to that in Fig. 5a. In general, drop dispersions are still enhanced. In contrast, the total concentration $N_{d(s)}$ is very similar to N_d because even though a significant fraction of particle size categories does not grow to droplet sizes, these do not contribute significantly to the total concentration. Both these methods of distributing FFC do have in common the fact that the FFC breaks the monotonic dependence of drop radius on particle size.

5. Discussion

The results show that even small amounts of FFC can have a significant effect on drop spectral evolution, and that the extent and nature of this effect depends on the distribution of this FFC among the particles. For a surface area weight distribution of FFCs onto the particles, the effects are quite marked and result in both enhancement in D and reduction in N_d. If FFC comprises a constant mass fraction of the particles, then the effects are diminished; enhancement in D is weaker and suppression of N_d is nonexistent.

An interesting inference from our simulations is that if our representation of the effect of FFCs is true to the natural process, there is not necessarily a monotonic relationship between the size of an aerosol and the size of a condensation drop (see also, Podzimek and Saad 1975). We are not aware of observational evidence that this simulated effect is a real one. We do suggest that a variable percentage concentration of soluble material in the CCN and/or variability in the hygroscopicity of particles could also create a similar situation. When one considers that complexity in the composition of aerosol is a likely feature of natural aerosol, we believe that this lack of monotonicity in the droplet size CCN relationship should not be surprising.

a. Broadening

When the FFC material is concentrated near the surface modal radius, a significant percentage of particles is prevented from growing into droplets during the early stages of cloud formation. The result is that the largest particles combine with the smallest activated particles to form the initial drop spectrum. Only later, when monolayers break down, do the midsize particles join the spectrum. In doing so they create a rather broad, flat spectrum below the spectral mode that is sometimes observed in FSSP measurements. If FFCs are prevalent, and if our simulations mimic their behavior somewhat realistically, one may not need to look to other theories such as entrainment mixing to explain the observed enhancement in breadth, particularly in adiabatic cores of clouds that are unaffected by mixing. This is clearly not proof that the observed spectrum flatness is related to the presence of FFCs, but it is not inconsistent.

Figure 2 shows that D_s/D decreases with increasing N_a but increases with increasing r_g, σ, and w. Analysis shows that this behavior is related to a number of factors, none of which is alone sufficient to explain the trends. The complexity arises from the fact that an increase in D_s/D may result from a decrease in D or an increase in D_s, for an incremental change in lognormal parameter or w. Three factors have been identified.

1) Retardation in the growth of some droplets and the associated enhancement in the maximum supersaturation

The decrease in D_s/D with increasing N_a (Fig. 2), is associated with an increase in D with increasing N_a that is faster than the increase in D_s with increasing N_a. When N_a is higher, the same amount of condensed water is distributed among more droplets, drops grow less, and there is less spectral narrowing through condensation

growth.[3] Figure 5c demonstrates this by contrasting observations of a narrow drop spectrum formed in relatively clean air with a broader spectrum formed in relatively polluted air. Because $N_{d(s)}$ is biased low relative to N_d (Fig. 2), D_s is biased low relative to D (for a given N_a). This effect is enhanced by the fact that the higher supersaturations in FFC simulations accelerate the growth of a smaller number of droplets, with attendant narrowing of the spectrum. The net result is that D_s/D decreases with increasing N_a, although in the mean it is always >1.

2) The increasing proportion of larger particles with increasing r_g and σ

Increases in r_g typically result in increases in D_s/D (Fig. 2), and these are due to increases in D_s that are more significant than the increases in D. An increase in r_g and/or σ increases the fraction of larger particles, which comprise larger amounts of soluble material. Therefore when FFCs are present the growth limitations are alleviated by the existence of larger particles. The large particles enhance the probability that particles coated with films will eventually break their monolayers and grow to droplet sizes—the primary broadening mechanism identified here.

3) Narrower spectra associated with higher w

An increase in w produces narrower spectra, regardless of FFC effects (e.g., Hudson and Yum 1997). When w is larger, there is less time available for particles (particularly the larger ones) to approach their equilibrium sizes at ambient relative humidity. At high w, when FFCs are present, supersaturations build up higher than they would in the absence of FFCs. The stronger driving force for growth increases the probability that monolayers will break and droplets will form. This effect counters the tendency to narrowing usually associated with increasing w. Therefore, decreases in D_s with increasing w are not as marked as decreases in D, and the ratio D_s/D increases with increasing w.

b. Suppression of N_d

Suppression in N_d is significant when the FFC is weighted by spectral surface area. The suppression in N_d derives from the retarded growth of a significant fraction of the particle population, as well as to the evolution of the supersaturation field. Although many of the particles near the surface-modal radius eventually do grow to droplet sizes once their monolayers have broken, this occurs at a stage when the supersaturation is rapidly decreasing, with the result that some of them never attain droplet sizes.

Figure 8 shows drop concentration versus N_a for various combinations of modified condensation coefficient α, as well as percent mass of FFC for the surface area–weighted distribution of FFC. Clearly, suppression of drop concentration increases with increasing FFC amount, as well as with decreasing α. For example, a 5% FFC mass contribution combined with a modified $\alpha = 10^{-5}$ yields a similar suppression to the case when the FFC mass contribution is 2%, but $\alpha = 10^{-6}$. When the modified $\alpha = 10^{-4}$, and the FFC mass contribution is 5% (line not shown), the power-law fit shows no change in the slope of the line compared to the case with no FFC. In this case, a significantly higher mass of FFC ($>10\%$) is required to produce a noticeable suppression in drop number.

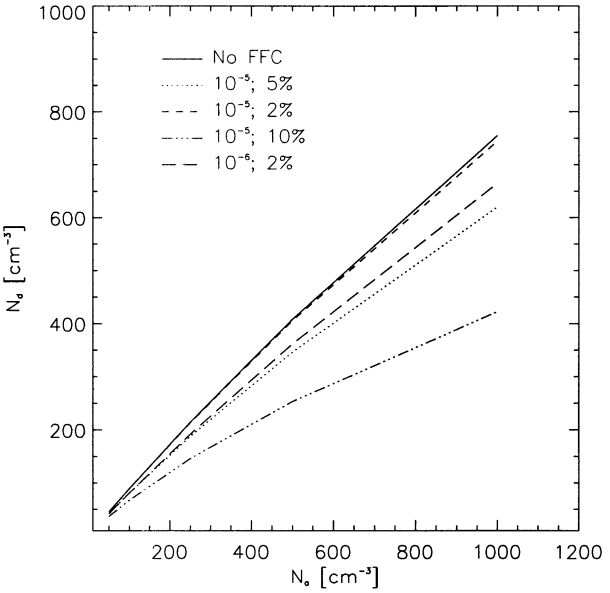

FIG. 8. Drop number concentration N_d as a function of aerosol concentration N_a for a range of α and percent contribution of FFC to total aerosol mass. FFC is weighted by surface area.

The reduction in N_d due to the existence of organic FFCs simulated here is opposite in trend to results that simulate the reduction in droplet surface tension due to the presence of organics (Facchini et al. 1999), and enhancement in N_d. We have not attempted to evaluate the relative importance of these processes. Whether organics ultimately enhance or reduce N_d is possibly case-dependent and worthy of further investigation.

6. Summary

Our simple model suggests that the effect of FFCs on drop spectral broadening is a function of both the total mass of FFC, and how it is distributed among the particles. In general, the effect is maximal when smaller, numerous particles are prevented from activating until they have grown sufficiently to remove a monolayer coverage of FFC. Their delayed activation results in drop spectra that comprise a mode of larger drops that grew earlier and had sufficient time to grow to appreciable sizes, together with

[3] Note that if collision-coalescence were active, spectra formed in cleaner air would be broader than those formed in polluted air.

a smaller mode of drops that activated later due to FFC growth retardation. The effect on drop spectral dispersion is significant and may result in an enhancement in dispersion of greater than 10 fold.

Film-forming compounds may also have a strong effect on cloud droplet number concentration. Because growth is inhibited, N_d tends to be reduced, particularly at larger aerosol median size and spectral breadth. The result is a saturation in N_d with increasing N_a that is qualitatively similar to observed saturation in N_d versus N_a (e.g., Chuang et al. 2000; Martin et al. 1994). The tendency for a reduction in N_d due to the existence of organic FFCs is opposite in trend to that caused by their reduction in droplet surface tension (Facchini et al. 1999) and enhancement in N_d. This paper has not attempted to evaluate the relative importance of these processes. In this regard, we do note that the Second Aerosol Characterization Experiment (ACE-2) dataset suggests that a standard parcel model of droplet growth (i.e., one that does not simulate reduction in surface tension or FFC growth retardation) tends to overpredict N_d (Chuang et al. 2000; Snider and Brenguier 2000; R. Wood 2002, personal communication). The effect of FFCs, as modeled here, does at least act in the direction of reducing drop number concentrations, but whether FFCs are indeed responsible for this disparity between model and observations remains an open question. This is exacerbated by the fact that the instrument used in these observations may saturate at high aerosol concentrations.

To the extent to which our results represent natural cloud processes, they may represent an important factor in the aerosol–cloud–climate problem. Enhancement in drop dispersion aids the formation of larger drops that initiate collision coalescence and precipitation. The depletion of cloud water by precipitation has consequences for cloud radiative effects that are so much a part of the climate system. The feedback of precipitation to atmospheric dynamics is also important. In nonprecipitating clouds, a suppression of cloud droplet number would result in less reflective clouds (for an equivalent liquid water content), and this too could have climatic consequences. As an example, simulations in Figs. 6a and 6b yield visible cloud optical depths of about 13 for the case without FFC, and 11 with FFC, that is, a reduction of 15%. Calculations of cloud reflectance using a simple two-stream approximation yield a reduction in cloud reflectance of about 10%.

The current work is somewhat speculative in that much information is lacking about natural organic FFCs: their abundance, distribution among particles, and real effects on droplet growth are not well known. It should therefore be viewed as an exploratory study and as an attempt to consider the conditions under which FFCs are likely to be important. The true effect will only become clearer as our knowledge of FFCs improves. It is our hope that the findings reported herein will serve as motivation for further experimental investigations in this field.

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